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WM2014 Conference, March 2-6, 2014, Phoenix, Arizona, USA**Development and Initial Testing of Off-Gas Recycle Liquid from the WTP Low Activity Waste Vitrification Process - 14333**

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ABSTRACT

The Waste Treatment and Immobilization Plant (WTP) process flow was designed to pre-treat feed from the Hanford tank farms, separate it into a High Level Waste (HLW) and Low Activity Waste (LAW) fraction and vitrify each fraction in separate facilities. Vitrification of the waste generates an aqueous condensate stream from the off-gas processes. This stream originates from two off-gas treatment unit operations, the Submerged Bed Scrubber (SBS) and the Wet Electro spray Precipitator (WESP). Currently, the baseline plan for disposition of the stream from the LAW melter is to recycle it to the Pretreatment facility where it gets evaporated and processed into the LAW melter again. If the Pretreatment facility is not available, the baseline disposition pathway is not viable. Additionally, some components in the stream are volatile at melter temperatures, thereby accumulating to high concentrations in the scrubbed stream. It would be highly beneficial to divert this stream to an alternate disposition path to alleviate the close-coupled operation of the LAW vitrification and Pretreatment facilities, and to improve long-term throughput and efficiency of the WTP system. In order to determine an alternate disposition path for the LAW SBS/WESP Recycle stream, a range of options are being studied.

A simulant of the LAW Off-Gas Condensate was developed, based on the projected composition of this stream, and comparison with pilot-scale testing. The primary radionuclide that vaporizes and accumulates in the stream is Tc-99, but small amounts of several other radionuclides are also projected to be present in this stream. The processes being investigated for managing this stream includes evaporation and radionuclide removal via precipitation and adsorption. During evaporation, it is of interest to investigate the formation of insoluble solids to avoid scaling and plugging of equipment. Key parameters for radionuclide removal include identifying effective precipitation or ion adsorption chemicals, solid-liquid separation methods, and achievable decontamination factors. Results of the radionuclide removal testing indicate that the radionuclides, including Tc-99, can be removed with inorganic sorbents and precipitating agents. Evaporation test results indicate that the simulant can be evaporated to fairly high concentration prior to formation of appreciable solids, but corrosion has not yet been examined.

INTRODUCTION

The Hanford LAW Recycle stream will be generated in the WTP by condensation and scrubbing of the LAW melter off-gas system by a SBS and WESP, as shown in Figure 1. This stream, which will contain substantial amounts of chloride, fluoride, ammonia, and sulfate ions, will get recycled within the WTP process by return to the Pretreatment Facility where it will be combined with the LAW stream and evaporated. The halide and sulfate components are only marginally soluble in glass, and often dictate the waste loading. Additionally, long-lived Tc-99 and I-129 are volatile radionuclides that accumulate in the LAW system, and are challenging to

incorporate in glass under the Hanford LAW melter operating conditions. Because Tc-99 has a very long half-life and is highly mobile [1, 2], it is the largest dose contributor to the Performance Assessment (PA) of the Integrated Disposal Facility (IDF) [3], although it is largely retained by the glass. Diverting this LAW Off-Gas Condensate stream to an alternate disposal path would have substantial beneficial impacts on the cost, life cycle, and operational complexity of WTP.

The objective of this development task is to evaluate (1) suitability of this stream to evaporation and tank farm storage (Figure 2), and, (2) decontamination of this stream using sorbents and precipitating agents (Figure 3). The latter process would be comparable to the Actinide Removal Process (ARP) at SRS that has been operating successfully for years. The concept for this decontamination process adapts the use of precipitating agents or sorbents, such as monosodium titanate (MST), to decontaminate the stream to enable alternative disposition. Implementation would make available both a short-term disposition path if the LAW facility commences operation prior to operation of the Pretreatment facility and a long term path to divert the stream from recycling.

Simplified Low Activity Waste Off-gas System

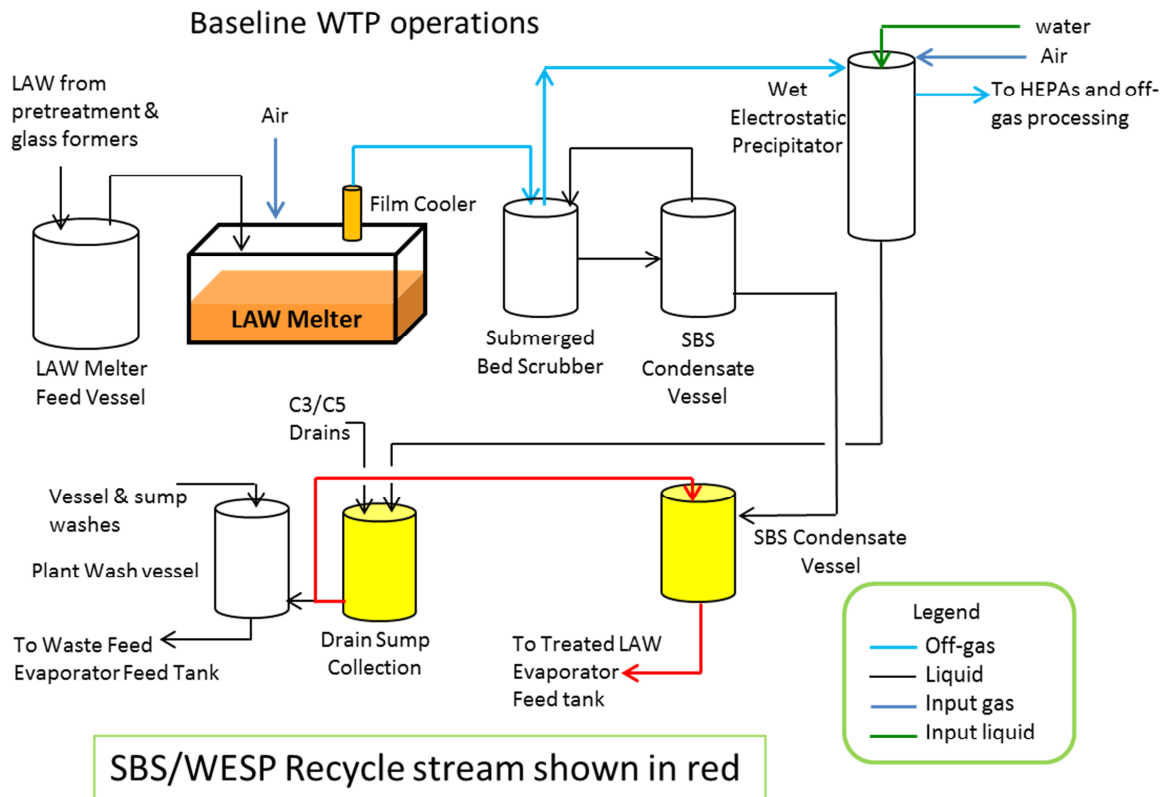


Figure 1. Simplified Low Activity Waste Off-gas System schematic

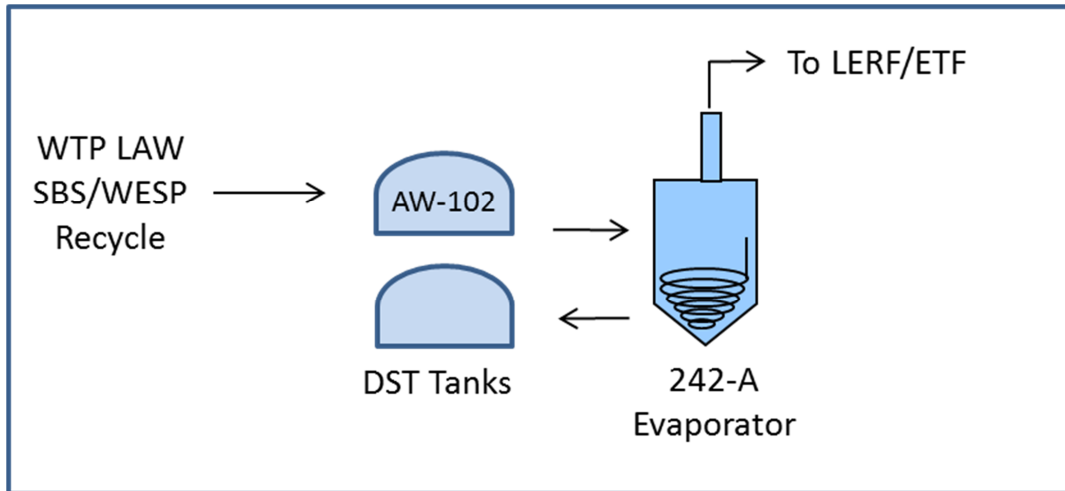


Figure 2. Schematic of evaporation and storage of Off-Gas Condensate in tank farms

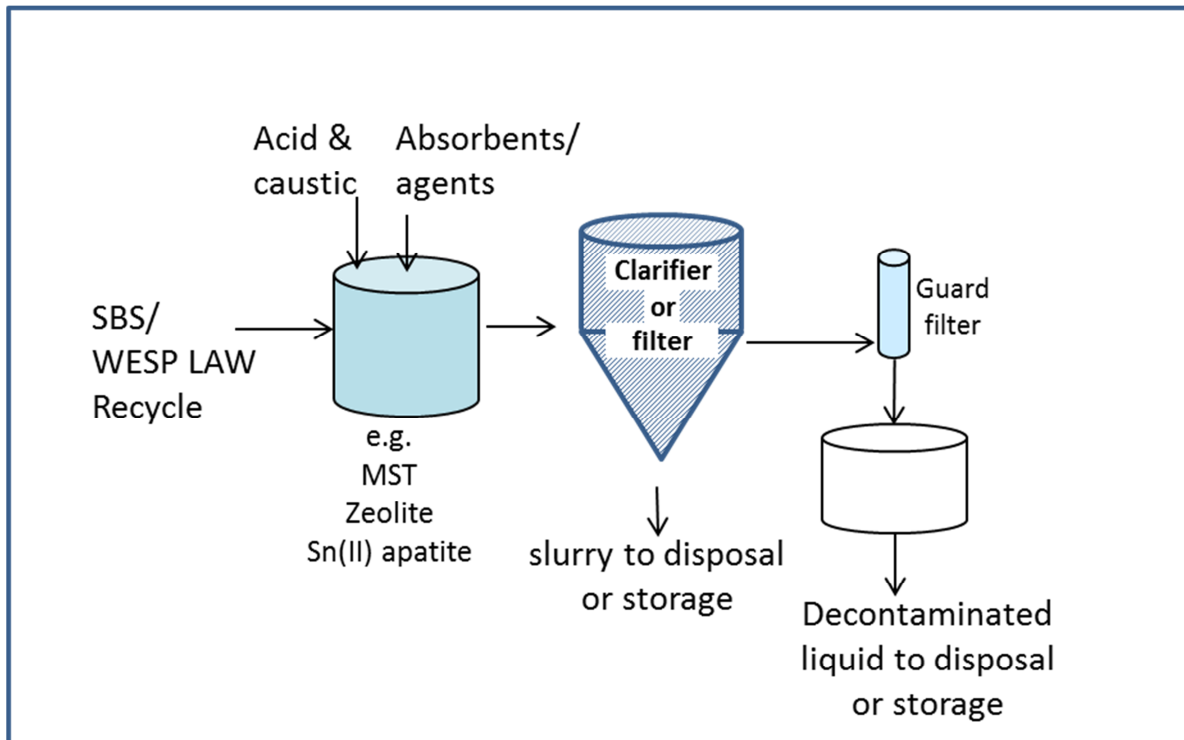


Figure 3. Off-Gas Condensate decontamination process schematic

Simulant Formulation Basis

Because this stream is not yet available for characterization, the simulant formulation was based on input from two sources. The projected solution chemistry and radionuclide content were based on version 7.4 of the Hanford Tank Waste Operations Simulator (HTWOS) modeling of the flow sheet [4] performed by Washington River Protection Solutions [5]. Insoluble solids

composition was primarily based on analysis of LAW Recycle obtained from pilot-scale simulant melter testing [6]. Basing the solution chemistry and radionuclide content on the computer modeling rather than melter testing results allowed evaluation of process conditions for treatment of all tank wastes, and accounts for internal WTP process streams. Since the computer model does not account for physical carryover of material, the insoluble solids used were based on test results. Results from pilot-scale melter off-gas system testing indicated that the solids were primarily glass formers because the solids were observed to contain iron and other components not typically in the aqueous LAW. Glass formers were added as the solids to the simulant formulation.

The radionuclide contents were based on the HTWOS model calculations. Radionuclides selected for inclusion in the simulant were based on a comparison to the Liquid Effluent Retention Facility and Effluent Treatment Facility (LERF/ETF) limits [7] as an example of a potential disposition path.

Evaporation and Storage

If the LAW Facility starts up first, concentration of this waste stream may be needed to accommodate its storage in the Tank Farms [8]. This is because the WTP will produce more aqueous waste volume than it treats, but with much lower activity and ionic strength, and there may be insufficient storage capacity for it, depending on several factors. Evaporation has a long history of successful operation on dilute, low-activity waste streams at both SRS and Hanford. However, evaporator fouling and scaling can occur when glass-formers are present, depending on the waste composition.

Using an evaporator for this concentration step has been discussed [8, 9], and for this task, it is assumed that evaporation in the 242-A evaporator would require first sending the Off-Gas Condensate to the Double Shell Tank (DST) system for storage. It is expected that caustic and nitrite will be added to comply with tank corrosion chemistry requirements. Two scenarios were tested: (1) where the LAW Recycle, including insoluble solids, is first adjusted for corrosion control; and (2) where the LAW Recycle is filtered from the insoluble solids, and evaporated at neutral pH. These scenarios are consistent with anticipated conditions for evaporation in 242-A and an auxiliary evaporator, respectively. Testing for evaporation in this phase was focused on solids formation and foaming.

One option that has been previously evaluated is disposal of the LAW Recycle stream directly to the ETF. This option has a number of consequences to ETF including increases in waste volume, halide levels and radioactivity [10, 11]. Sending this stream to ETF would cause both the halide and radionuclide concentrations to increase substantially, challenging existing treatment capabilities [11]. If the radionuclides are removed from the Recycle stream in an alternate process and the decontaminated liquid was then sent to the ETF or an alternate disposal path, the fluoride, sulfate, and chloride would be purged from the LAW system, yielding substantial benefits to WTP and mitigating the consequences of radioactive contamination. Testing was performed at SRNL to examine both evaporation and radionuclide removal.

Radionuclide Removal Process

In addition to Tc-99, other radionuclides have either volatile forms (e.g. I-129) or are carried over as particulates from the melter into the off-gas system, or some combination of both mechanisms. For this proposed alternative treatment process, separation of the radionuclides is done by precipitation or sorption onto pre-formed materials and settling and/or filtration. Emphasis was on using entirely inorganic materials to enable easier storage and disposal as immobilized waste. For technetium removal, these materials included reducing agents (e.g. Sn(II) or Fe(II) compounds) coupled with absorbents (e.g. hydroxyapatite). The Sn(II) with hydroxyapatite and oxalate has previously been found effective for precipitating Tc from water samples [12]. For cesium removal, the primary material tested was zeolites. The strontium and actinide removal was examined using the same MST used at SRS ARP.

For this proposed alternative treatment process there is no defined decontamination factor requirement established. At this stage, radionuclides that are in appreciable quantities will be removed by the currently available technology to the extent practical.

EXPERIMENTAL

Simulant Preparation

Detail on the basis and synthesis of the simulant has been documented [13]. The target concentrations of chemicals and radionuclides were derived from the output from the HTWOS calculation, documented in SVF-2732 [5]. The aqueous phase was prepared from dissolution of laboratory chemicals, as shown in Table I. A single batch of 3.5 L of simulant (i.d.: SBS Sim. batch 3) was prepared and used for the sorbent/reagent tests. The glass formers were then added, and mixed for five days at ambient temperature of ~ 23 °C. The filtrate pH was measured to be 8.2 after mixing and was slightly adjusted to a pH of 7.3 ±0.3 with ~ 50 drops of concentrated nitric acid.

TABLE I. Aqueous simulant formulation

Chemical	Formula	Mass (g)/L simulant
Aluminum nitrate nonahydrate	Al(NO ₃) ₃ ·9H ₂ O	0.400
Sodium chromate	Na ₂ CrO ₄	0.283
Potassium chloride	KCl	0.219
Sodium chloride	NaCl	1.395
Sodium fluoride	NaF	3.209
Ammonium nitrate	NH ₄ NO ₃	4.760
Sodium nitrate	NaNO ₃	1.221
Sodium nitrite	NaNO ₂	0.016
Ammonium sulfate	(NH ₄) ₂ SO ₄	3.220
Dibasic sodium phosphate dihydrate	Na ₂ HPO ₄ ·2H ₂ O	0.040

The glass formers added to the simulant are shown in Table II, based on the projected composition [14]. Sucrose was excluded because it is destroyed in the melter and would not impact results here because it would not be present in the off-gas condensate stream.

TABLE II. Glass formers

Mineral	Formula	Mass (g)/L simulant
kyanite	Al ₂ SiO ₅	0.745
borax	Na ₂ B ₄ O ₇ ·10H ₂ O	0.0123
boric acid	H ₃ BO ₃	1.430
wollastonite	CaSiO ₃	0.772
iron oxide (hematite)	Fe ₂ O ₃	0.430
lithium carbonate	Li ₂ CO ₃	0.392
forsterite olivine	Mg ₂ SiO ₄ -Fe ₂ SiO ₄	0.257
sodium carbonate	Na ₂ CO ₃	0.003
silica	SiO ₂	2.857
rutile	TiO ₂	0.114
zinc oxide	ZnO	0.286
zircon	ZrSiO ₄	0.372
sucrose	C ₁₂ H ₂₂ O ₁₁	0
	Total	7.67

The neutralized simulant containing the glass formers was stirred for several days at room temperature. The solids were then removed by filtration with a 0.45- μ m Nalgene filter. A 1-L portion of the filtrate was then spiked with the radioisotope tracers.

Simulant Evaporation

The neutral pH simulant was prepared (3.0 L) for evaporation by first filtering it (Nalgene 0.45- μ m) to remove insoluble solids. For the alkaline evaporation test, the simulant (including glass formers) was prepared (3.0 L) for evaporation by first adjusting with sodium nitrite and sodium hydroxide to meet the Hanford tank waste storage requirement. Sodium nitrite was added to reach 0.07 M nitrite, and sodium hydroxide to raise the pH to 12.6. The adjusted solution was agitated for 5 days; and the pH was monitored to ensure it did not fall below pH = 12. The adjusted solution was then filtered to remove insoluble solids, and the filtrate solution was sampled for analysis.

The vacuum evaporator test apparatus is shown in Figure 4. In the two evaporator campaigns (neutral and alkaline pH), the filtrate was loaded into the evaporator pot. The volume of the first batch was 400 mL. Pressure was adjusted to 60 torr, and the hot plate and magnetic stir-bar were turned on. The solution boiled at approximately 42 °C. After collecting 250 mL of condensate, an additional 250 mL of filtrate was added via suction line to the pot to maintain the liquid level. This cycle was repeated until the 3 L of simulant was almost entirely evaporated. Condensate was periodically removed by breaking vacuum and emptying the condensate collection vessel. Concentrate samples were targeted for collection at the first visible solids (“pre-7.5X), 7.5X, 18X, 24X, and 30X (each concentration calculation accounted for the withdrawal of the preceding periodic samples). The actual concentration points where samples were collected are shown in Table III. The final concentration in the evaporator pot was ~30X.

TABLE III. Evaporation sampling matrix

Sample Name	Neutral Campaign Calculated Concentration	Alkaline Campaign Calculated Concentration
Pre-7.5X	11.0	3.4
7.5X	7.0	7.3
18X	16.6	17.5
24X	22.1	23.3
30X	27.6	29.1

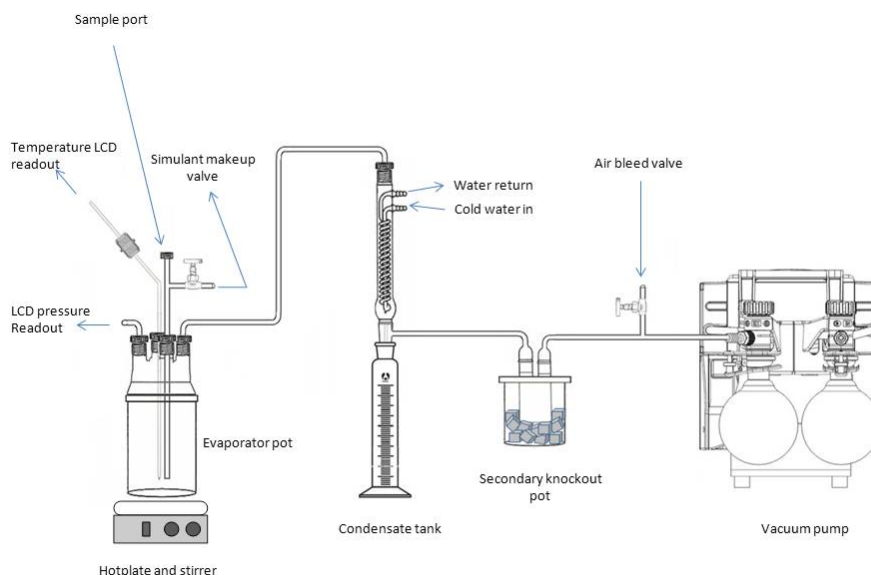


Figure 4. Evaporator apparatus diagram

Simulant Spiking with Radionuclides

A 1-L sample of the filtrate was spiked with the radiotracer solutions shown in Table IV. After stirring for ~6 days, the 1-L batch was filtered with a 0.45- μm Nalgene filter. A small amount of white solids were observed. The filtrate was then analyzed for radionuclide contents.

TABLE IV. Radiotracer solutions added to 1-L of simulant

Isotope	Matrix	Amount	Target concentration (dpm/mL)
Cs-137	Cs-137 in 0.1 M HCl	35 μL	1.16E4
U-238	UO ₂ (NO ₃) ₂ ·6H ₂ O solid	0.00188 g	6.24E-1
Pu-239	1.5 g/L WG Pu in 0.45 M HNO ₃	0.4 μL	6.95E1
Sr-85	Sr-85 radionuclide in 0.5 M HCl	68 μL	5.79E4
Tc-99	Ammonium pertechnetate solution	109 μL	9.21E4

Sorption/Precipitation Tests

In general, tests were performed by adding a small amount of sorbent/reagent to a poly bottle, followed by the addition of 20 mL of the radioactive simulant solution, as shown in Table V. The bottle was then agitated in a shaker oven at ~25 °C for the specified time (the Tc reduction tests were sampled at two time points). Each sample was then filtered through a 0.1-µm filter. The filtrate was then analyzed for the radionuclide of interest.

TABLE V. Sorbent/reagent test matrix

Sorbent/Reagent	Mass Phase ratio	Target quantity	Matrix	Target Duration (hours)
Cs Removal				
Ionsiv [®] IE-95	100:1	10 g/L	Dry solid	48
CST (Ionsiv [®] IE-911)	100:1	10 g/L	Dry solid	48
Sr/Actinide Removal				
MST	5000:1	0.2 g/L	14.7 wt% aqueous slurry	24
Tc Removal				
Sn(II) & hydroxyapatite	167:1	3 g/L SnCl ₂ 3 g/L hydroxyapatite	Dry solid	2, 18
Sn(II) & Na-oxalate	167:1	3 g/L SnCl ₂ 3 g/L Na ₂ C ₂ O ₄	Dry solid	2, 18
IS-MIO	5000:1	0.1 g/L Fe(II) 0.1 g/L Fe(III)	0.5 M FeSO ₄ 0.5 M Fe ₂ (SO ₄) ₃ 0.2 M H ₂ SO ₄	2, 18
pH =12 adjusted Separations				
pH 12 Ionsiv [®] IE-95	100:1	10 g/L	Dry solid	48
pH 12 MST	5000:1	0.2 g/L	14.7 wt% slurry	24
pH 12 Sn(II) & hydroxyapatite	167:1	3 g/L SnCl ₂ 3 g/L hydroxyapatite	Dry solid	2, 18
pH 12 ISMIO	5000:1	0.1 g/L Fe(II) 0.1 g/L Fe(III)	0.5 M FeSO ₄ 0.5 M Fe ₂ (SO ₄) ₃ 0.2 M H ₂ SO ₄	2, 18

The sources of the sorbents and precipitation reagents were:

IE-95: UOP Ionsiv[®] IE-95, 20x50 mesh (commercial zeolite)

CST: Crystalline Silicotitanate, UOP Ionsiv[®] IE-911, (not caustic washed) (commercial zeolite)

MST (NaTi₂O₅·xH₂O): 14.7 wt% aqueous slurry, Optima

Tin(II) chloride dihydrate (SnCl₂·2H₂O): Fisher chemical

Hydroxyapatite (Ca₅(PO₄)₃OH): Aldrich chemical

Sodium oxalate (Na₂C₂O₄): Aldrich chemical

IS-MIO (In-situ Mixed Iron Oxide) was prepared by dissolving iron (II) sulfate heptahydrate in 0.4 M H₂SO₄ to prepare a 1 M solution. A 1 M iron (III) sulfate solution was then prepared by

dissolving iron (III) sulfate hydrate in distilled water. Just prior to use, equal volumes of each solution were combined to give a 1 M solution of Fe in 0.2 M H₂SO₄.

A second set of tests was performed after pH adjustment of the simulant. The simulant (250 mL subsample) was adjusted to pH 12.0 using ~3.1 – 3.2 g of 50 wt% sodium hydroxide solution. The simulant was not filtered prior to contact with the sorbents/reagents, but a control sample was filtered and analyzed to examine the effect of the pH adjustment without any sorbents/reagents. The absorption/precipitation tests were then repeated with the pH-adjusted solution. The mixtures were then filtered, followed by analysis of the filtrate.

RESULTS AND DISCUSSION

Results of the duplicate chemical analysis of the neutralized, filtered simulant used for precipitation testing are shown in Table VI. Similar results were obtained for the simulant batches used for evaporation. These match the target composition reasonably well, although more ammonium was added than the target (~ 18% higher than the ‘Average’ case and ~ 9% higher than the ‘Maximum’ case from SVF-2732). The presence of boron, lithium, silicon, and zinc are due to dissolution of the glass former solids.

TABLE VI. Neutralized simulant filtrate chemical composition

Component	Concentration (mg/L)	Standard Deviation	Component	Concentration (mg/L)	Standard Deviation
Al	<0.100		Si	52.7	0*
B	253	8	Ti	<0.100	
Ca	<0.100		Zn	28.6	0.2
Cr	91.0	0.4	Zr	<0.100	
Fe	<0.100		F ⁻	1.25E3	7
K	150	1	Cl ⁻	934	5
Li	80.3	0.4	NO ₂ ⁻	<10	
Mg	<0.100		NO ₃ ⁻	4.90E3	21
Na	2980	0*	SO ₄ ⁻²	2.41E3	0*
P	<10.0		PO ₄ ⁻³	<10	
S	832	5	NH ₄ ⁺	1770**	

*Standard Deviation of zero indicates the two analysis results were identical

**analysis of single sample

Decontamination Tests

Results of the radionuclide analysis results on the initial spiked filtered simulant are shown in Table VII. Results of the Sorbent/Reagent tests are shown in Tables VIII and IX.

TABLE VII. Initial simulant radionuclide composition

Isotope	Concentration (dpm/mL)	Reported Method Uncertainty
Cs-137	2.50E4	5.0%
U-238	6.09E-1	20%
Pu-239	3.91E1	9.0%
Sr-85	5.18E4	5.0%
Tc-99	9.93E4	20%

TABLE VIII. Summary of results of sorbent/reagent tests (Neutral pH).

Sorbent/Precipitating Agent	MST	IE-95	CST (IE-911)	Sn(II) & Hydroxyapatite		Sn(II) & Na-oxalate		IS-MIO	
				1.98	18.2	2.00	18.2	1.98	18.2
Contact Time (h)	24.2	48.0	48.1	1.98	18.2	2.00	18.2	1.98	18.2
Avg. Sr DF	1.29 (0.01)	21.5 (1.70)	44.9 (22.7)	NM	1.64 (0.12)	NM	1.27 (0.09)	NM	2.58 (0.18)
Avg. Cs DF	0.99 (0.00)	4.32 (0.01)	3.35 (0.57)	NM	0.97 (0.07)	NM	0.98 (0.07)	NM	0.99 (0.07)
Avg. Pu DF	> 1.8 [†]	6.29 (4.05)	> 6.00	NM	6.15 (2.01)	NM	0.12* (0.02)	NM	3.13 (1.13)
Avg. Tc DF	0.99 (0.02)	1.00 (0.28)	1.01 (0.28)	>577	> 577	84.2 (4.17)	50.7 (11.9)	0.99 (0.00)	1.08 (0.00)
Avg. U DF	2.25 (0.51)	2.86 (0.81)	2.31 (0.65)	1.82 (0.03)	2.07 (0.04)	1.01 (0.03)	1.03 (0.04)	0.97 (0.01)	0.98 (0.02)
Avg. Cr DF	NM	NM	NM	NM	10.1 (1.47)	NM	5.65 (0.81)	NM	1.49 (0.21)

[†]Duplicate measurements gave very different values, one falling below the method detection limit (DF values of 1.82 and >9.17); *evidently, the Pu analysis was in error

Notes: 1) Outlined boxes indicate target sorbates for each material. 2) Values in parentheses represent either the standard deviation from duplicate measurements or the method uncertainty for single measurements (italicized values). 3) NM = not measured.

TABLE IX. Summary of results of sorbent/reagent tests (pH 12).

Sorbent/Precipitating Agent	MST	IE-95	Sn(II) & Hydroxyapatite		IS-MIO	
			1.94	18.0	1.93	18.0
Contact Time (h)	24.0	48.0	1.94	18.0	1.93	18.0
Avg. Sr DF	319 (10.4)	5.32 (1.26)	NM	7.17 (0.51)	NM	> 774
Avg. Cs DF	1.01 (0.01)	17.9 (2.39)	NM	1.05 (0.07)	NM	1.03 (0.07)
Avg. Pu DF	11.6 (12.1)	18.4 (6.85)	NM	2.41 (0.38)	NM	> 9.96
Avg. Tc DF	1.00 (0.02)	0.98 (0.28)	3.35 (0.03)	3.62 (0.10)	1.12 (0.01)	1.13 (0.00)
Avg. U DF	10.5 (0.54)	> 40.3 (11.4)	3.02 (1.00)	2.29 (0.45)	5.28 (0.44)	21.2 (3.27)
Avg. Cr DF	NM	NM	NM	5.78 (0.82)	NM	1.44 (0.20)

Notes: 1) Outlined boxes indicate target sorbates for each material. 2) Values in parentheses represent either the standard deviation from duplicate measurements or the method uncertainty for single measurements (italicized values). 3) NM = not measured.

In general, the performance of the sorbent materials was greatly influenced by the pH of the simulant. The Sr and actinide removal performance of MST increased as the pH was increased from 7.3 to 12.0. This was most noticeable for Sr removal, where the MST DF increased from 1.3 to greater than 300. At neutral pH the Ionsiv[®] IE-95 appeared to slightly outperform the CST (Ionsiv[®] IE-911) for Cs removal, and the performance of the Ionsiv[®] IE-95 increased by a factor of ~4 as the pH was increased to 12. This is consistent with the conversion of ammonium ion, which was expected to interfere with Cs removal on zeolites, to ammonia, which should minimally interfere. The Ionsiv[®] IE-95 also showed significant affinity for the actinides at pH 12, with DF values higher than those obtained with MST, although this is not a direct comparison because the Ionsiv[®] IE-95 had 50 times the amount of sorbent and longer contact duration.

The Sn(II) reducing agent coupled with hydroxyapatite sorbent worked extremely well for Tc removal at neutral pH. The Sn(II) hydroxyapatite system removed essentially all of the Tc (to below a method detection limit of 5 µg/L) within 2 hours. Using sodium oxalate as a sorbent was less effective. The Tc removal performance was greatly reduced at a pH of 12.0. The IS-MIO did not appear to be an effective Tc removal agent at either pH, but did show excellent Sr and actinide removal at pH 12. This is consistent with previous work showing IS-MIO was effective for removing Sr and actinides from SRS HLW [15]. As expected, the Sn(II) reductions caused precipitation of chromium, presumably due to reduction of Cr(VI) to Cr(III).

Removal of Pu and U were more effective at pH 12, with the Ionsiv[®] IE-95 than with the MST at the sorbent concentrations tested. This result suggests that MST would not be needed, if Ionsiv[®] IE-95 is used under alkaline conditions for cesium removal.

Evaporation Tests

The solution was successfully evaporated to the target concentration. Density of the slurry increased as the evaporation proceeded, as shown in Figure 5 for the first campaign (neutral pH) and second campaign (alkaline pH). At neutral pH, other than the final, 30X samples, only small amounts of insoluble solids were observed in evaporator pot samples. The solids were found to contain fluoride and sulfate, present as the kogarkoite (Na₃F(SO₄)). Additional solids formed at 30X concentration, as seen in Figure 6, which shows the XRD of the final solids. The results indicate that the insoluble solids are <1 wt% in all but the final, 30X sample at neutral pH. At alkaline pH, substantially more solids were observed. The 24X sample contained substantial amounts of solids, primarily kogarkoite. The solution in the evaporator pot was observed to become turbid by the time the solution reached 7.5X for both the neutral pH and alkaline test.

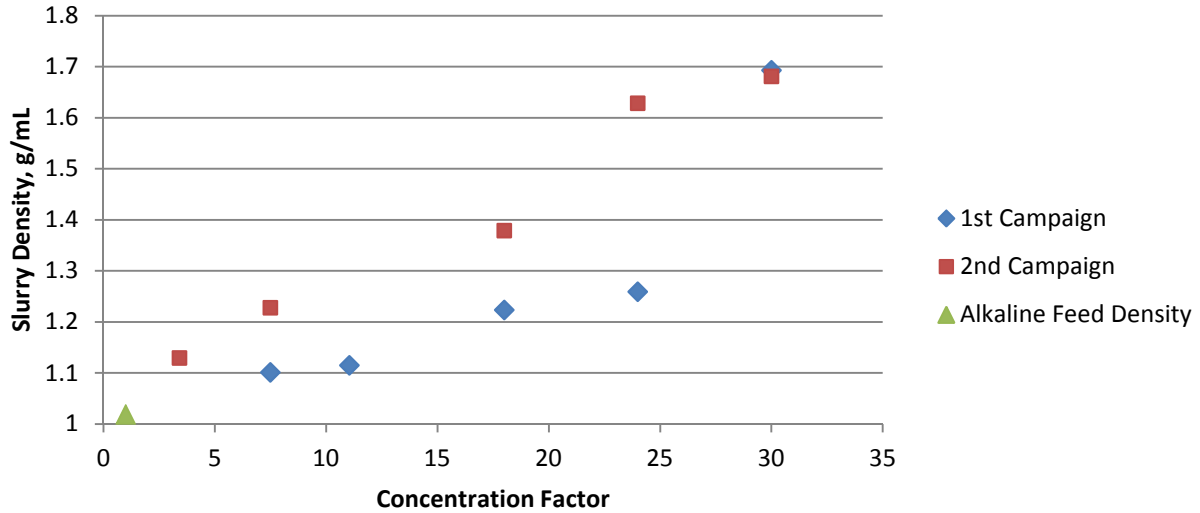


Figure 5. Evaporator pot sample density versus concentration factor

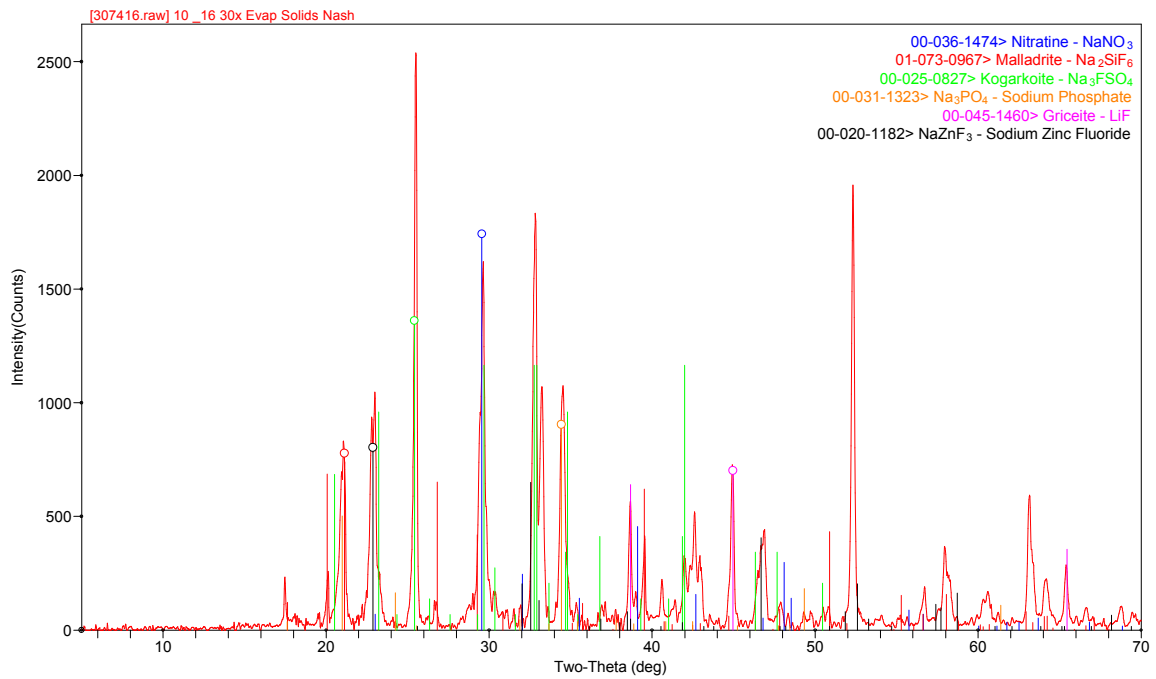


Figure 6. X-Ray Diffraction pattern of solids from 30X sample of neutral evaporation campaign

CONCLUSIONS

Sorption testing with various inorganic sorbents and precipitating agents proved successful for the removal of target sorbates. As expected, the performance of the materials was found to be dependent upon the pH of the simulant. The Sn(II) was much more successful at removal of Tc under near neutral conditions, whereas, the inorganic sorbents (MST and Ionsiv[®] IE-95) worked

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much better at pH 12. The Ionsiv[®] IE-95 was more effective than MST for Sr and actinide removal at neutral pH, and was better for actinides at pH 12. Since the target DF for the average waste composition for Sr was 1 (i.e., no removal for the average), Ionsiv[®] IE-95 may be adequate for decontaminating this waste stream for Sr and actinides. Additional testing with ²⁴¹Am is needed, however, to determine if MST is needed. All radionuclides were removed to some extent under the conditions tested. Good decontamination was achieved for all radionuclides in at least one test condition.

Evaporation of the simulant was successful at identifying approximate concentration factors that could be achieved without producing substantial solids. Small amounts of solids were observed in the evaporator pot at 7.5X for both neutral and alkaline conditions. Substantial amounts of solids (>1 wt%) were observed at 24X for the alkaline condition and 30X for the neutral condition. The solid most commonly found was kogarkoite [Na₃F(SO₄)].

FUTURE WORK

Additional work is needed to further optimize the conditions needed for increased removal, and to further define the DF targets. This preliminary test indicates that the most challenging radionuclide, Tc-99, is easily removed. This removal was done in two hours using reducing agents without special inerting controls to prohibit oxygen or manipulation of temperature. Although the chromium was also removed, the total amount of chromium present is small, and could likely be accommodated in the final waste form.

Although the DF for Cs-137 was not as high as expected, some manipulation of the parameters would likely improve the removal. Raising the pH slightly higher may have some benefit, or switching to Ionsiv[®] IE-911 at pH 12 may be sufficient.

Although the optimal pH for removal of Tc is neutral and for removal of Sr and actinides is alkaline, this does not preclude a work-able process. Presumably, the Tc removal with Sn(II)-hydroxyapatite could be performed at neutral pH, followed by pH adjustment and contact with Ionsiv[®] IE-95 or IE-911. It is likely that solid-liquid removal between the steps would not be needed, although it has not been demonstrated that pH adjustment after removal of Tc would not partially reverse the Tc removal. A single solid-liquid separation of the Sn(II)-hydroxyapatite and Ionsiv[®] sorbent may suffice. Testing of the sequential concept is needed, along with optimization of the reagent addition, contact durations, measurement of the distribution coefficients, and demonstration of a coupled process. Once these parameters are better defined, testing would be needed on disposition of both the slurry and aqueous phases. Examination of Am-241 removal is also needed, but this is likely achievable with MST or one of the Ionsiv[®] materials.

REFERENCES

1. Icenhower, J.P., Qafoku, N.P., Martin, W.J., Zachara, J.M., The Geochemistry of Technetium: A Summary of the Behavior of an Artificial Element in the Natural Environment, PNNL-18139, December 2008

WM2014 Conference, March 2-6, 2014, Phoenix, Arizona, USA

2. Icenhower, J.P., Qafoku, N.P., Martin, W.J., Zachara, J.M., The Biogeochemistry of Technetium: A review of the behavior of an Element in the Natural Environment, American Journal of Science Vol. 310(8):721-752, October 2010
3. Mann, F.M., Puigh, R.J., Khaleel, R., Finfrock, S., McGrail, B.P., Bacon, D.H., Serne, R.J., Risk Assessment Supporting the Decision on the Initial Selection of Supplemental ILAW Technologies, RPP-17675, Rev. 0, September 29, 2003
4. Belsher, J.D., Empey, P.A., Hohl, T.M., Kirkbride, R.A., Ritari, J.S., West, E.B., Bergmann, L., M., Wells, M.N., Hanford Tank Waste Operations Simulator (HTWOS) Version 7.4 Model Design Document, RPP-17152, Rev. 7, November, 2012
5. SVF-2732, 2013, "SVF-2732 MMR-13-008 data Case 1 rev 0.xlsx," Rev. 0, Washington River Protection Solutions, LLC, Richland, Washington.
6. Matlack, K.S., Gong, W., Diener, G., Bardakci, T., Brandys, M., Pegg, I.L., Final Report; Summary of DM1200 SBS History and Performance, VSL-066410-2, August 2, 2006
7. McCabe, D.J., Wilmarth, W.R., Nash, C.A., Waste Treatment Technology Process Development Plan for Hanford Waste Treatment Plant Low Activity Waste Recycle, SRNL-STI-2013-00351, July, 2013
8. Crawford, T.W., Conner, J.M., Johnson, M.E., Mann, F.M., Unterreiner, B.J., Williamson, R.D., Lueck, K.J., McNamar, E.A., Secondary Waste Management Strategy for Early Low Activity Waste Treatment, RPP-RPT-37924, July, 2008.
9. Yanochko, R.M., Corcoran, C., Golcar, G.R., Johnson, P., Nolan, L.M., Pajunen, A., Submerged Bed Scrubber Condensate Disposal Preconceptual Engineering Study, RPP-RPT-52321, September, 2012
10. Lueck, K.J., Mcnamar, E.A., Low Activity Waste (LAW) Facility Secondary Waste to Effluent Treatment Facility (ETF) Treatability Evaluation, HNF-37718, May, 2008
11. May, T.H., Gehner, P.D., Stegen, G., Hymas, J., Pajunen, A., Sexton, R., Ramsey, A., Secondary Waste – ETF Pre-Conceptual Engineering Study, RPP-RPT-43588, December 22, 2009
12. Moore, R.C., Holt, K.C., Zhao, H., Hasan, A, Hasan, M, Bontchev, B., Salas, F, Lucer, D., Anionic Sorbents for Arsenic and Technetium Species, SAND2003-3360, September 2003.
13. Adamson, D.J., Nash, C.A., McCabe, D.J., Crawford, C.L., Laboratory Testing of Hanford Waste Treatment Plant Low Activity Waste Recycle Simulant, SRNL-STI-2013-00713
14. Arakali, V., Stone, I., 2012 WTP Tank Utilization Assessment, 24590-WTP-RPT-PE-12-001, Rev. 0, March 26, 2012

WM2014 Conference, March 2-6, 2014, Phoenix, Arizona, USA

15. Poirier, M. R.; Herman, D. T.; Burket, P. R.; Peters, T. B.; Serkiz, S. M.; Fink, S. D., Testing of the In Situ, Mixed Iron Oxide (IS-MIO) Alpha Removal Process, WSRC-TR-2004-00283, Rev. 0, June, 2004.